

PATENT ABSTRACTS OF JAPAN

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(54) NON-AQUEOUS SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a non-aqueous secondary battery having extremely high charge/discharge capacity.

SOLUTION: An electrode active material capable of storing and releasing lithium ions comprises SiO_x having an x-value of less than 1.00. Particularly, the SiO_x (the x-value being preferably less than 2.00) is preferably subjected to hydrofluoric acid treatment. An electrode and the non-aqueous secondary battery each comprise using the electrode active material.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the electrode active material which uses a nonaqueous electrolyte for an electrolysis solution and is used for a negative electrode and/or an anode at the nonaqueous secondary battery and it using the material which can emit [occlusion and] a lithium ion.

[0002]

[Description of the Prior Art]In recent years, the demand over a small rechargeable battery is increasing with the spread of a notebook computer or cellular phones. As for the rechargeable lithium-ion battery which used the multiple oxide for positive active material, and used a carbonaceous material or metallic oxides, such as black lead, for negative electrode active material, active research is done with the outstanding characteristic and safety.

[0003]

[Problem(s) to be Solved by the Invention]The maximum charge-and-discharge capacity of the rechargeable battery which used carbonaceous materials, such as black lead, for negative electrode active material is 372 mAh/g, and is small as compared with the case where metal lithium is used. Then, the metallic oxide containing the metal which forms lithium and a metal alloy is proposed (refer to JP,10-284056,A), and it came to reveal high charge-and-discharge capacity by this as compared with the carbonaceous material.

[0004]On the other hand, through the old experiment, this invention persons understood the tendency for charge-and-discharge capacity to become high, so that x value of SiOx was small. However, since SiOx currently indicated in the above was manufactured using the gaseous phase method, it did not happen easily that x value becomes less than 1.00, and it had not been realized that x value uses less than 1.00 SiOx as an electrode active material.

[0005]This invention is made in view of the above, and the purpose is to provide the electrode active material for nonaqueous secondary batteries. It is that charge-and-discharge capacity provides the nonaqueous secondary battery which is size very much using the electrode active material.

[0006]

[Means for Solving the Problem]That is, this invention is an electrode active material which can emit [occlusion and] a lithium ion, wherein x value consists of SiOx which is less than 1.00, and this especially SiOx is obtained by a fluoric acid approach. This invention is an electrode or a nonaqueous secondary battery characterized by coming to use the above-mentioned electrode active material. x value applicable to manufacture of an electrode active material of the above [this invention] is a manufacturing method of less than 1.00 SiOx.

[0007]

[Embodiment of the Invention]Hereafter, it explains in more detail about this invention.

[0008]x value of the electrode active material used by this invention is less than 1.00 SiOx.

[0009]SiOx of this invention ~ the mass ratio of powdered Si and O ~ FESEM/EDS (an energy dispersion type X-rays detector.) For example, when it considers that it measures using the JEOL Co., Ltd. make, it is converted into a mole ratio, and it is a compound of the empirical formula SiOx. The x value is 0.10-1.00, and when ESCA analysis (X-ray photoelectron spectroscopy "ESCA750", for example, Shimadzu production) is moreover conducted, it is defined as Si and SiO2 being a substance which has a peak in a different position.

[0010]As a synthesizing method of SiOx of this invention, although there are no restrictions in particular, the way x value processes 1.00 or more SiOx(es) by fluoric acid, for example is mentioned. Namely, as indicated by JP,3-72008,B and JP,4-29603,B, the solid state SiO, SiO2, and Si, or, mixing, being filled up in a reactor and heating at not less than 1400 **. Inactive gas like Ar and reducing gas like H2 are supplied, SiO gas is generated, and it is obtained by carrying out secondary treatment of SiOx (x value is less than 2.00) which caught the particles which cooled and generated it, or the commercial SiOx.

[0011]It filters, after 0.1~s10 times the amount's adding and stirring fluoric acid solution for 1 to 120 minutes with fluoric acid mass to SiOx (x value is less than 2.00) as a method of processing by fluoric acid as secondary treatment. The residue on a filter paper is often washed until filtrate shows neutrality, and less than 1.00 SiOx is obtained for x value. When a fluoric acid addition is less than 0.1 time, in less than 1 minute, less than 1.00 SiOx is not obtained [mixing time] for x value. On the other hand, if churning time performs superfluous processing exceeding 120 minutes when a fluoric acid addition exceeds 10 times the amount or, the yield of SiOx of x value made into the purpose will fall remarkably.

[0012]Unprecedented big charge-and-discharge capacity was actually obtained by making x value of SiOx into less than 1.00. x value is so desirable to improvement in discharge-and-charge capacity that it is small. Although the occlusion and the discharge mechanism of the Li ion as an electrode active material of SiOx are not known well, SiOx was returned to Si at the time of early charge and discharge, it was presumed that the reversible reaction of Li occurred between the Si and Li, and it is guessed in SiOx of this invention that it is because the content of relative Si [in / as compared with 1.00 or more SiOx(es) / in x value / SiOx] increased.

[0013]Although the electrode active material of this invention can be used also as which active material of an anode or a negative electrode, using as negative electrode active material is more preferred.

[0014]When it uses as negative electrode active material, as positive active material, The metallic sulfide or the metallic oxide which does not contain lithium, such as general TiS₂, MoS₂, NbSe₂, and V₂O₅, the lithium multiple oxide which makes a subject Li_xMO₂ (however, M is one or more kinds of transition metals, and x values are usually 0.05-1.0.) -- cobalt acid lithium, manganic acid lithium, etc. are specifically used.

[0015]When the active material of this invention is used as positive active material, as negative electrode active material, base metals, such as Li, can generally be used.

[0016]The electrode used for the nonaqueous secondary battery of this invention can be manufactured by distributing the mixture of the negative electrode active material or positive active material which consists of the above-mentioned SiOx powder, and a conducting agent into the fluid containing a binder, preparing a slurry, and applying and drying it at the collecting electrode plate which consists of metallic foils.

[0017]As a binder used for the electrode of the nonaqueous secondary battery of this invention, Poly polyethylene, nitrile rubber, polybutadiene, isobutylene-isoprene-rubber, polystyrene, styrene-butadiene rubber, polysulfide rubber, nitrocellulose, tetrafluoroethylene resin, polyvinylidene fluoride, chloroprene, fluoridation is used.

[0018]Especially as a collecting electrode plate used for the electrode of the nonaqueous secondary battery of this invention, although not limited, the metallic foil of alloys which make these an ingredient, such as gold, silver, copper, platinum, aluminum, iron, nickel, chromium, manganese, lead, tungsten, and titanium, is used. The thinner one of the thickness of a metallic foil is preferred. Aluminum is liked by the anode from the ease of handling, copper is liked by the negative electrode, and it is used.

[0019]In order to produce the nonaqueous secondary battery of this invention, in the cell which consists of a conventional anode, negative electrode, and electrolysis solution and which is constituted, what is necessary is just to use the negative electrode and/or anode of SiOx powder content concerning this invention instead of a negative electrode and/or an anode, and a special thing is not required.

[0020]As an electrolysis solution, propylene carbonate, ethylene carbonate, gamma-butyrolactone, N-methyl pyrrolidone, acetonitrile, N,N-dimethylformamide, Dimethyl sulfoxide, a tetrahydrofuran, 1,3-dioxolane, methyl formate, sulfonate, oxo ZORIDON, a thionyl chloride, 1,2, - dimethoxyethane, diethylene carbonate, these derivatives, etc. are used. As an electrolyte, the halogenide of lithium, the perchlorate of lithium, the thiocyanogen salt of lithium, the Howe fluoride salt of lithium, the Lynn fluoride salt of lithium, the arsenic fluoride salt of lithium, the aluminum fluoride salt of lithium, trifluoromethyl sulfate of lithium, etc. are used. Parts, such as a separator, a terminal, and an electric insulating plate, are attached if needed.

[0021]Shape of the nonaqueous secondary battery of this invention can be used as a coin type, a core box, a paper type, a card shape, etc., and is portable sized electronic equipment, such as a video camera, a personal computer, a word processor, and a cellular phone, etc. as a use.

[0022]

[Example]Hereafter, an example and a comparative example are given and this invention is explained still more concretely.

[0023][Examples 1-3] [Comparative example 1]

Having been filled up with the mixture of commercial SiO₂ powder and metal Si powder in the reactor, and heating it at not less than 1400 **, Ar was supplied, SiO gas was generated, the powder which cooled and generated the gas was caught, and x value obtained SiOx of 1.07. The capacity which shows fluoric acid solution for the quantity which shows the obtained SiOx powder in Table 1 in Table 1 5% to a balance, **, and it was added, and it filtered, after stirring for 15 minutes, respectively. The residue on a filter paper was often washed until filtrate showed neutrality with 150 ml of pure water. The physical properties of the obtained sample are shown in Table 1. What does not perform fluoric acid processing processing was used as the comparative example 1.

[0024]After mixing with acetylene black (conducting agent), using obtained SiOx as an active material, The slurry that the solution containing PVDF (polyvinylidene fluoride: binder) would be distributed, and SiOx powder, black lead, and PVDF would be 45%, 40%, and 15%, respectively was prepared, it was applied and dried at copper foil (collecting electrode plate), and the electrode was produced.

[0025]What dissolved with a molar concentration of 1 LiPF₆ in the solution which mixed ethylene carbonate/dimethyl carbonate by half of volume ratios was used as the electrolysis solution, using metal lithium as an anode, the coin type cell was produced, and the charge and discharge test was done.

[0026]The test condition was performed to metal lithium by 0-1.0V and constant current 1.06 A/g (it is 3.2 mA to 3 mg to an active material). The maximum service capacity is shown in Table 1.

[0027]

[Table 1]

	SiO _x 量 (g)	フッ酸濃度 (mol)	SiO _x / HF比	x (SiO _x)	最大放電容量 (mAh/g)
実施例1	1.0	100	5.0	0.44	1395
実施例2	1.5	90	1.7	0.71	1058
実施例3	5.0	50	0.5	0.90	830
比較例1	—	—	—	1.02	666

[0028]

[Effect of the Invention]According to this invention, the electrode active material which can emit [occlusion and] Li ion is provided, and the nonaqueous secondary battery with which charge-and-discharge capacity becomes by using the electrode active material further in size is provided.

[Translation done.]